

# Porous chromatographic materials as substrates for preparing synthetic nuclear explosion debris particles

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**Abstract** Several porous chromatographic materials were investigated as synthetic substrates for preparing surrogate nuclear explosion debris particles. Eighteen metals, including some of forensic interest, were loaded onto materials by immersing them in metal solutions (556 mg/L of each metal) to fill the pores, applying gentle heat (110 °C) to drive off water, and then treating them at high temperatures (up to 800 °C) in air to form less soluble metal species. High-boiling-point metals were uniformly loaded on spherical controlled-pore glass to emulate early fallout, whereas low-boiling-point metals were loaded on core-shell silica to represent coated particles formed later in the nuclear fallout-formation process. Analytical studies characterized material balance and the formation of recalcitrant species. Metal loading was 1.5–3 times higher than expected from the pore volume alone, a result attributed to surface coating. Most metals were passively loaded; that is,

solutions filled the pores without active metal discrimination. However, niobium and tin concentrations were lower in solutions after pore filling, and were found in elevated concentrations in the final products, indicating selective loading. High-temperature treatments caused reduced solubility of several metals, and the loss of some volatile species (rhenium and tellurium). Sample preparation reproducibility was high (the inter- and intra-batch relative standard deviations were 7.8 and 0.84 %, respectively) indicating suitability for use as a working standard for analytical methods development. We anticipate future standardized radionuclide-loaded materials will find use in radioanalytical methods development and/or serve as a starting material for the synthesis of more complex nuclear explosion debris forms (e.g., Trinitite).

**Keywords** Synthetic nuclear explosion debris · Nuclear forensics · Trace metals analysis · Controlled-pore glass · Core-shell silica · Matrix sequestration

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## Introduction

Nuclear explosion debris is a highly unique environmental sample formed under extreme conditions. Temperature and pressure within a nuclear detonation fireball can reach tens of millions of degrees and millions of pounds per square inch, respectively. The composition of the fallout material produced depends on weapon design, energy yield, proportion of fission energy, height of the blast, and the terrain below the blast [1]. Fallout particles present a diverse array of different morphologies. Although particles are usually spherical, fused and irregular particles are formed as well. Particles are typically solid; however, particles with gas bubbles/inclusions have also been reported [2, 3].

Whether the fireball impacts the surface below the blast has a major effect on fallout composition. For air-burst detonations, in which the fireball does not impact the surface, volatilized material includes bomb and encasement components as well as fission and activation products of these materials. Particulate matter is formed from condensation of the volatilized material as the nuclear fireball cools. For air bursts, small particles (0.01–20  $\mu\text{m}$ ) are formed that travel long distances before settling [1]. The situation becomes far more complex when low-altitude or ground bursts are considered. In this case the blast cloud not only contains the components found in an air burst, but also volatilized terrain materials, solid terrain particulate matter, and activation products derived from these materials [1]. It is estimated that a 1-megaton ground detonation could entrain 300,000 tons of dust [4]. Overall, the fallout particles formed from a ground- or low-altitude burst range in diameter from large (marble-sized) to sub-micron. As the fireball begins to cool, the vaporized surface material condenses along with the less volatile radionuclides, forming larger particles that have uniformly distributed refractory radionuclides [1]. In addition, particulate ground materials that were never completely vaporized in the fireball will serve as nuclei for metal condensation, forming particles that are coated on the surface with relatively volatile radionuclides. Metals that condense on the cooling particles tend to remain localized on the surface as coatings because penetration into the particle core is hindered once the temperature cools to less than about 1,400  $^{\circ}\text{C}$  [3]. The majority of fallout from a low-altitude or ground burst consists of coated particles [1].

Elemental fractionation occurs during fallout genesis because the less volatile radionuclides condense first on larger particles associated with close-in early fallout. The more volatile elements condense on the smaller particles that remain after the cloud begins to cool. Condensation of nonvolatile products produced by decay of gaseous detonation products also leads to elemental fractionation. Isotopic fractionation also can occur during the particle genesis process because of differences in isotope boiling points [1].

Archived nuclear debris collected during World War II weapon testing programs is not appropriate for developing analytical methodologies because of the severely limited quantities that are available and the absence of short-lived isotopes. The research described herein is one approach being pursued to synthesize materials that closely mimic the morphological and other properties (e.g., elemental, isotopic, chemical composition of key isotopes of interest, etc.) of actual nuclear explosion debris. The results reported are based on condensed-phase methods, whereas other approaches being pursued are based on high-temperature, gas-phase or plasma-based metal deposition approaches. Together, these approaches will enable the creation of a

diverse suite of surrogate materials designed to closely mimic a wide range of nuclear debris types.

In general, current analytical protocols often use target analytes spiked on matrix surfaces followed by isolation and quantification. This approach gives information on matrix-specific analyte recovery as well as the reproducibility of the extraction and analysis technique. Although this approach has become standard practice in many analytical methods, several significant shortcomings are evident. Actual environmental contaminants undergo transformations and incorporation into the sample matrix during the aging process, and therefore display different properties when subjected to analytical interrogation compared to surface-spiked surrogates [5, 6]. For this reason, techniques that incorporate radionuclides into the surrogate debris matrix would be preferred over surface-spiked approaches.

The objective of this study was to investigate the novel use of porous chromatographic materials for producing nuclear fallout surrogate material. Chromatographic applications of metal-loaded porous supports have been extensively studied. Early studies investigated gas-phase retention of hydrocarbons and catalytic transformation on porous stationary supports that contain metal oxides [7]. Other studies focused on gas-phase retention of Lewis bases on supports that contain metal complexes [8]. Condensed-phase separations also have used metal-loaded silica to provide selectivity (i.e., argentation chromatography) [9, 10]. Although the vast majority of materials developed by the chromatographic community are used for separations, novel applications for these materials continually emerge. A few unique applications of porous chromatographic materials are cited below as a brief cross section of the numerous examples. Porous clay materials have been used for evaporative cooling to condition room air since ancient times and are currently used in roof construction for similar reasons [11]. High-capacity porous materials have been used for carbon dioxide sequestration as well as hydrogen storage [12]. Porous catalytic coatings are widespread, having been designed for a number of diverse goals including bioanalytical applications that encompass a broad range of tissue engineering applications [13], use as enzyme activity enhancers [14], and use as drug delivery vehicles [15, 16]. Porous silica glasses also have been used as matrices for immobilization of nuclear waste [17]. The study reported herein expands this list to include preparation of synthetic nuclear explosion debris particles.

This research synthesizes simulant particles with properties that mimic various nuclear explosion debris fallout particles. The desired material will allow more realistic analytical procedures to be developed for the analysis of actual nuclear explosion debris than would be permitted by the traditional surface-spiked approach. The studies presented here focus on the material loading and

characterization aspects using stable isotopes, and will set the stage for future preparation of radioactive debris particles and composite materials.

A number of substrates were investigated for particle synthesis in the current study: (1) irregular controlled-pore glass (CPG); (2) spherical CPG; and (3) core–shell silica materials. Eighteen metals were studied, some of which are relevant to nuclear forensics; additional metals will be added in future studies. The isotopically natural metals were loaded onto materials in aqueous solutions, the water was evaporated from the pores using gentle heat, and the deposited pore-bound and surface metals immobilized by high-temperature treatment in an air environment. The resulting particles were then dissolved or leached followed by analysis of the solutions for metals by inductively coupled plasma (ICP)/optical emission spectrometry (OES) to give insight into the mass balance and degree of metal immobilization, respectively. The materials produced also were characterized by a variety of additional analytical means, including Raman spectrometry, scanning electron microscopy (SEM), and wavelength dispersive spectroscopy (WDS). These studies are requisite for further studies that include incorporating metals that are either radioactive or can be made radioactive by neutron activation. Application of porous chromatographic materials as substrates for synthesis of surrogate nuclear detonation debris particles is a novel application area that has not been previously described.

## Materials and methods

### Chemicals

Metal standards were obtained from Inorganic Ventures (Christiansburg, VA, USA) as either 10,000 or 1,000 mg/L solutions. Hydrofluoric acid was purchased from Sigma-Aldrich (St Louis, MO, USA), along with nitric and hydrochloric acids (Ultrax brand). A standard of  $\text{Co}_3\text{O}_4$  was prepared for Raman spectroscopy by placing 300  $\mu\text{L}$  of the 10,000 ppm cobalt metal standard (i.e., cobalt nitrate) in a quartz crucible and heating in air at 650 °C overnight to form a dark-colored film.

Three porous chromatographic materials were investigated as substrates during this study. The physical characteristics of these materials are compiled in Table 1 for easy reference. The materials included two CPGs. The first CPG consisted of irregular particles (#CPG500C) obtained from Millipore (Billerica, MA, USA). This CPG has a mean pore size of 548 Å, a pore size distribution of  $\pm 2.5\%$ , a pore volume of 1.18 cc/g, a surface area of 49.5  $\text{m}^2/\text{g}$ , and particle size diameters ranging from 74 to 149  $\mu\text{m}$ . The second material was a spherical CPG obtained from VitroBio GmbH (Steinach/Thür, Germany). This material had a pore diameter of 487.5 Å, a pore volume of 1.735 cc/g, a surface area of 147.7  $\text{m}^2/\text{g}$ , and particle size diameters ranging from 50 to 100  $\mu\text{m}$ . The final material was core–shell silica (Kinetex, HELIC) that was purchased through special arrangement with Phenomenex (Torrance, CA, USA). The core–shell silica was monodisperse (2.6  $\mu\text{m}$  diameter) with a shell thickness of 0.35  $\mu\text{m}$ , a pore size of 88 Å, a density of 2.2 g/cc, and a pore volume of approximately 0.3 cc/g.

### Metal loading and immobilization procedures

Metal-loading studies used 10,000 mg/L element standards of the 18 metals listed in Table 2. Irregular CPG was loaded with a mixture of 16 of these metals. Silver and tin were excluded from this particular study because of compatibility issues that caused precipitation in the loading solution. The load solution was prepared by adding 278  $\mu\text{L}$  of each metal standard with 552  $\mu\text{L}$  of nitric acid to give 5.0 mL of a solution that contained 556  $\mu\text{g}/\text{mL}$  of each metal. Spherical CPG was loaded with 10 metals that generally had high boiling points. This load solution contained 278  $\mu\text{L}$  of each of the 10 metal solutions along with 552  $\mu\text{L}$  of concentrated nitric acid and 1,668  $\mu\text{L}$  of distilled water to give 5.0 mL of a load solution that contained 556  $\mu\text{g}/\text{mL}$  of each metal. The core–shell silica load solution contained 278  $\mu\text{L}$  of each of 10 mostly low-boiling metal standards along with 552  $\mu\text{L}$  of concentrated nitric acid and 1,668  $\mu\text{L}$  of distilled water to give 5.0 mL of a solution that contained 556  $\mu\text{g}/\text{mL}$  of each metal. This latter load solution

**Table 1** CPG and core–shell silica properties along with the theoretical metal loading expected exclusively from filling the pores compared to the actual loading observed on the materials

Material/property	Particle diameter ( $\mu\text{m}$ ) and shape	Pore size diameter (nm)	Pore volume (cc/g)	Surface area ( $\text{m}^2/\text{g}$ )	Theoretical load ( $\mu\text{g}/\text{g}$ )	Actual load ( $\mu\text{g}/\text{g}$ )
Irregular CPG	74–149 $\mu\text{m}$ , irregular	54.8 $\pm$ 2.5 %	1.18	49.5	656	~1,300
Spherical CPG	50–100 $\mu\text{m}$ , spherical	48.8	1.74	147.7	967	~1,450
Core–shell silica	2.6 $\mu\text{m}$ monodisperse, spherical	8.8	0.3	200	167	~500

Theoretical and actual load differences are thought to result from coating of the outer surfaces during filtration and drying

**Table 2** List of metals that were loaded on the different materials along with their boiling points

Metal	Boiling point (°C)	Irregular CPG	Spherical CPG	Core-shell silica
Cesium	678	×		×
Cadmium	765	×		×
Tellurium	990	×	×	
Barium	1,140	×		×
Strontium	1,394	×		×
Bismuth	1,560	×		×
Samarium	1,900	×		×
Silver	2,212			×
Tin	2,270			×
Gold	2,807	×	×	
Cobalt	2,870	×	×	×
Neodymium	3,127	×	×	×
Lutetium	3,315	×	×	
Lanthanum	3,469	×	×	
Zirconium	4,377	×	×	
Molybdenum	4,612	×	×	
Niobium	4,927	×	×	
Rhenium	5,627	×	×	

contained silver and tin, metals that were not represented in the other load solutions.

The loading procedure involved mixing 0.50-g CPG and the 5.0-mL load solution in a 15-mL Falcon tube and periodically agitating for 30 min. The material was then subjected to vacuum filtration through a 0.45- $\mu\text{m}$  Phenex Nylon filter (Phenomenex), and the particles were washed with 2.5 mL of fresh load solution. The material was then dried on the filter for 5 min (while vacuum was applied) before transferring to a Teflon watch glass where it was dried in air for an additional 5 min. The procedure for the core-shell material was similar except that a reduced quantity of material was processed (0.2 g), and the filter and room air-dry times were 20 min. After weighing, the materials were placed in a 110 °C oven overnight.

Metal immobilization on the material was accomplished by heat treatments. Aliquots (200 mg) of the oven-dried CPG and core-shell materials were placed in quartz crucibles and subjected to high-temperature treatments at 600 or 800 °C in a Lindberg Model 51848 furnace (Watertown, WI, USA) for either 24 or 72 h. The muffle furnace oven was heated or cooled slowly to the final temperatures over a period of 20–30 min to avoid thermal shock of the materials.

#### Raman analysis

Raman spectra were obtained using a DeltaNu Raman spectrometer, which consisted of an ExamineR 785 Raman module equipped with an Olympus BX51 microscope. A

785-nm, 120-mW laser served as the excitation source. The Raman backscattered light was detected on a charge-coupled device operated in dispersive mode. The spectrometer has a 5  $\text{cm}^{-1}$  spectral resolution. Various microscope objectives (10 $\times$ , 50 $\times$ , or 100 $\times$ ) were used, although the probe spot size was not determined.

#### Electron microscopic analysis

Samples were examined using a JEOL JSM-7001 Field Emission Scanning Electron Microscope. Samples were prepared for analysis by attaching them to carbon tape on aluminum stubs. Samples were coated with approximately 15 nm of pure carbon to prevent charging under the electron beam. Initial studies obtained secondary electron images using accelerating voltages of 10 and 15 kV. After imaging the samples, qualitative elemental energy dispersive X-ray spectrometry (EDS) analyses using an EDAX Apollo 40 Silicon Drift Detector (SDD) with EDAX Genesis Microanalysis Software were performed using an accelerating voltage of 20 kV and a collection time of approximately 100 s. The SDD allows the collection of high-count rates and superior light-element performance down to (and including) boron. To obtain quantitative compositional data, samples were analyzed using a JEOL JXA-8530F Electron Microprobe and WDS. Analysis was on 12–14 individual grains for each material using an accelerating voltage of 20 kV, a beam current of 22 nA, and a beam diameter of 1–2  $\mu\text{m}$ .

#### Dissolution and leach procedures

##### *Dissolution procedure*

Particle dissolutions were accomplished by heating weighed amounts ( $\sim 20$  mg) of particles ( $<100$  °C) with 1.5-mL concentrated hydrofluoric and 0.5-mL concentrated nitric acids in loosely capped 15-mL conical perfluoroalkoxy polymer (PFA) containers (Savillex, Eden Prairie, MN, USA). Once dissolved, the solutions were gently evaporated just to dryness, before adding 1.0 mL concentrated nitric acid and 0.5 mL of concentrated hydrochloric acid. These samples were diluted to 5.0 mL with 2 % nitric acid and the concentration adjusted accordingly prior to ICP/OES analysis. All dilutions were prepared by weight so that the total sample dilution factor was accurately known for use in calculating loading concentrations in the starting materials.

##### *Leach procedure*

Weighed quantities of the prepared materials were leached by one of four different solutions that varied in strength

from weak to strong. Leach solutions were (1) distilled water (weak leach), (2) 5 % nitric acid (moderate leach), (3) 5 % nitric acid/5 % hydrochloric acid (moderate leach), and (4) 50 % nitric acid (strong leach). Aliquots were removed from each leach solution after 1, 4, 24, and 48 h. Experiments were performed on 1.3–10 mg of material treated with 1.0 mL of each leach solution. At each time period, 100  $\mu$ L of the leach supernatant was removed and added to 4.9 mL of 2 % nitric acid, diluted appropriately, and then analyzed by ICP/OES.

#### ICP/OES analysis

Elemental analysis of the CPG total dissolution or leach solutions were made using a model ICAP 6500 Duo (Thermo-Fisher Corp., Cambridge, England) ICP-OES. Samples were typically diluted for a target element concentration between 0.1 to 10 mg/L. Two emission wavelengths were used for each element to check for potential interference. Instrument calibration was performed using a multi-element solution matched to the sample, prepared by weight dilution from 1,000 mg/L single element standards (Inorganic Ventures). The standard sample introduction system was employed with axial plasma viewing and ‘precision mode’ acquisition. Three repeat measurements were made for each sample with a typical relative standard deviation (RSD) less than 0.5 % observed, and a total acquisition time of about 3 min per standard or sample. Typical linear regression coefficients for the calibration plots were greater than 0.99. All metals could be determined using this approach, with the exception of cesium that displays only very weak emission lines.

## Results and discussion

CPGs were chosen for these studies because of their relatively large pore volumes, high structural stabilities, and the wide range of available particle and pore sizes [18]. In addition, because CPGs are available in both spherical and irregular particles, a variety of simulated debris morphologies can be produced. The extensive pore structure allows uniform filling with load solution that should lead to uniform metal composition throughout the particle. The irregular CPG was loaded with the broadest range of metals possible, whereas the spherical CPG was loaded with high-boiling-point metals to emulate fallout formed early in the particle-formation process. Core-shell silica was chosen as a substrate to synthesize coated particles that mimic debris formed later in the fallout-formation process when lower-boiling-point metals coat the outer surface of the cooling particles.

Boiling point was the principal property used to determine which metals were loaded on each different material. Another important consideration was stability of the

aqueous metal mixture. To be considered for this study, experiments were conducted to verify that load solutions showed no signs of precipitation for at least 3 h after mixing. The metal solutions presented in Table 2 meet or exceed this solution-stability requirement.

#### Identification of $\text{Co}_3\text{O}_4$ on heated metal-loaded CPG by Raman spectroscopy

Initial studies of the loaded irregular CPG material noted a dramatic change in color from white to dark purple upon heat treatment. This material was analyzed by Raman spectroscopy and the resulting spectra compared to literature values. Although other minor Raman bands were present, predominant Raman signals were present at 482, 620, and 690  $\text{cm}^{-1}$ . The observed spectrum gave an excellent match with literature spectra for  $\text{Co}_3\text{O}_4$  [19, 20]. This identification was further verified by matching the spectrum with a  $\text{Co}_3\text{O}_4$  standard prepared in our laboratory. Of the analytical techniques used to characterize the materials, Raman spectroscopy provides unique value because of its ability to determine speciation of the surface metals.

#### Electron microscopic analysis

The CPG materials were subjected to WDS to generate quantitative estimates of the metals obtained on the exterior surface of the material. At least 17 measurements for each CPG material were taken and the three measurements that came closest to giving the expected weight percent for the silicon content in silica (46 %) were averaged. These data are presented in Table 3 along with the detection limits for the WDS determinations. The detection limits provided by the instrument software are dependent on the sample matrix and the counts in both the standard and sample, as described Scott and Love [21]. With the exception of bismuth in the irregular CPG and rhenium in the spherical CPG, values determined were clearly above the detection limit. The standard deviations reported in Table 3 are for the three measurements and represent the variation in surface concentration encountered between the individual areas probed (i.e.,  $<3.1 \mu\text{m}^2$ ) during WDS analysis. The spherical CPG yielded some interesting results. The analysis for rhenium on the spherical CPG was below the detection limit, a result that could result from loss of volatile  $\text{Re}_2\text{O}_7$  (boiling point of 360  $^\circ\text{C}$ ) during the heat treatment. Large concentration values for gold resulted from occasional localized deposits on the surface that were clearly visible using secondary electron microscopic imaging.

The theoretical amounts of metal deposited in the pores, based on pore volume and load solution concentration,

**Table 3** WDS analyses of metal-loaded irregular and spherical CPGs that were heated at 800 °C for 72 h

Metal	Concentration on irregular CPG with standard deviation (wt%)		Concentration on spherical CPG with standard deviation (wt%)		Detection limits (wt%)
	Average ( $n = 3$ )	Standard deviation	Average ( $n = 3$ )	Standard deviation	
Cesium	–	–	–	–	–
Cadmium	0.28	0.20	–	–	0.15
Tellurium	0.58	0.23	0.51	–	0.06
Barium	1.78	1.92	–	–	0.08
Strontium	0.93	0.95	–	–	0.07
Bismuth	<0.18	–	–	–	0.18
Samarium	0.54	0.20	–	–	0.06
Gold	0.20	0.06	2.31	2.96	0.11
Cobalt	0.44	0.10	0.47	0.49	0.02
Neodymium	0.58	0.21	0.43	0.37	0.06
Lutetium	0.81	0.56	0.49	0.50	0.05
Lanthanum	0.76	0.52	0.41	0.34	0.10
Zirconium	0.70	0.22	0.91	0.83	0.10
Molybdenum	0.83	0.40	0.55	0.57	0.07
Niobium	0.40	0.18	0.48	0.24	0.09
Rhenium	0.44	0.44	<0.08	–	0.08

Over 17 measurements for each material were taken, the three analyses that gave silicon measurements closest to 46 wt% were averaged, and the standard deviation of the three values was determined. Detection limits are based on counting statistics and the quantity of analyte present in the materials

were 0.07 and 0.10 wt% for the irregular and spherical CPG, respectively. The values presented in Table 3 were consistently larger than theoretical values, possibly because of additional material surface coating the particles that is not taken into account in the pore volume. For the purposes of the subsequent discussion, we define the total material loading as a composite of metal deposited because of (1) pore filling and (2) coating on the outer surface of the material. It is possible that the surface coating that occurs during the filtering and drying steps deposit more metal per area on the outer surface of the material because the coating layer may be substantially thicker than is possible within the Å-sized pore dimensions.

#### Analysis of materials by total dissolution

##### *Irregular CPG*

Total dissolution studies were conducted to measure the amount of metals that were actually loaded on the different materials. Figure 1a shows the metal quantities obtained from ICP/OES analysis of the dissolved irregular CPG. The amounts are plotted relative to theoretical amount that would have been expected based solely on filling the pores with the load solution. The irregular CPG blank was clean and did not contain significant background of any of the metals of interest. The amounts of metals in the loaded irregular CPG were about twice what would have been predicted based on deposition of the metal in the CPG pores (Table 1). The most likely explanation for this result

is additional surface coating; an explanation that is consistent with the higher than expected wt% values observed by WDS analysis.

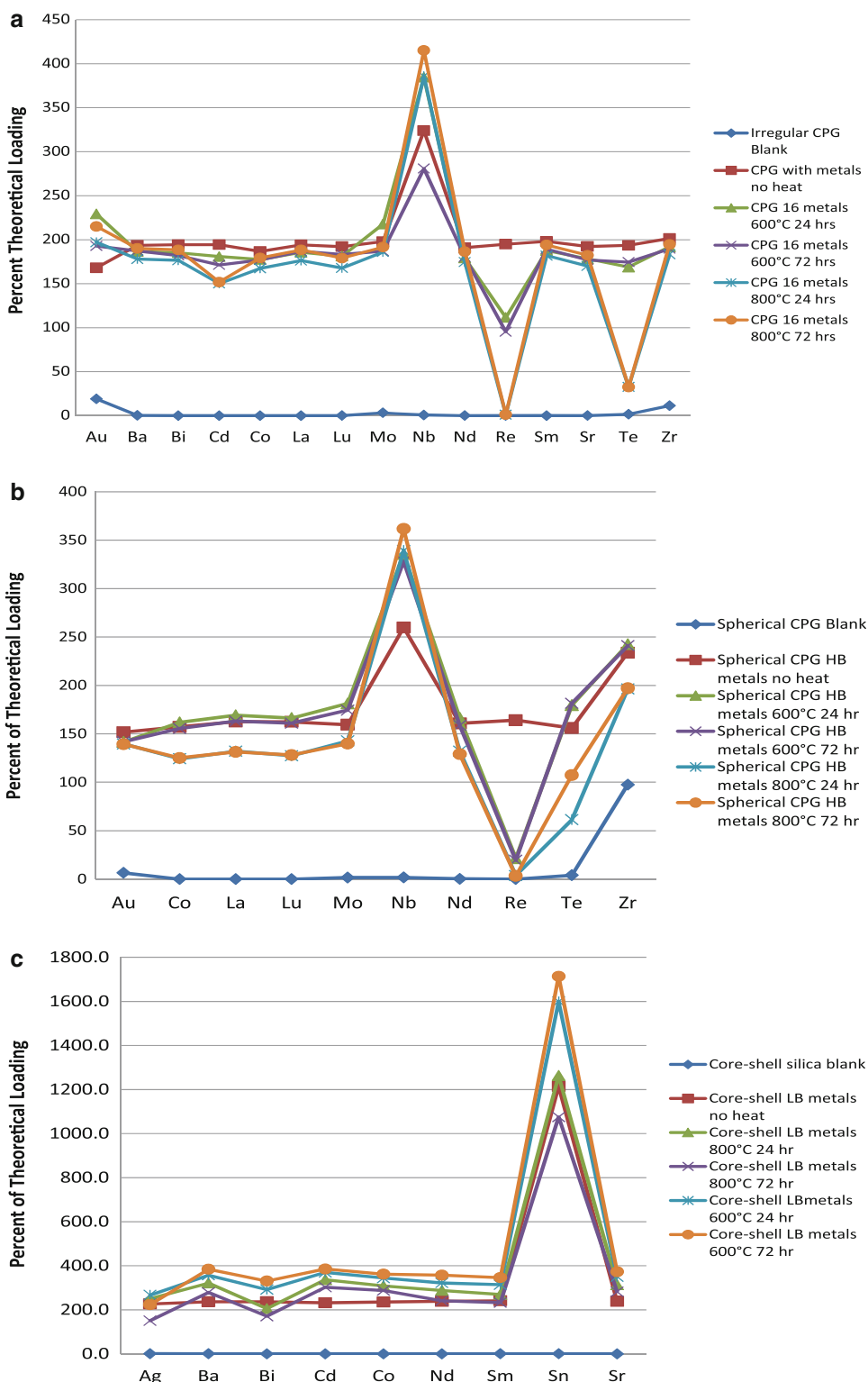
Several interesting trends were seen in these data. Most notable was the enhanced concentration of niobium relative to the other metals, a result that could be caused by selective loading. Powdered Vycor glass (a leached, highly porous borosilicate glass) is known to selectively remove niobium from acidic solutions of zirconium, a result similar to current observations [22]. Other metals were present at roughly equivalent concentrations in the unheated CPG. For rhenium, the concentration was dramatically reduced upon heating, with high losses occurring at higher temperature treatments. This indicated loss of a volatile species, in this case the most likely compound was  $\text{Re}_2\text{O}_7$ . Rhenium is often used in radiochemical studies as an analog for technetium, which also is known to form a volatile oxide upon heat exposure. Also of interest was the loss of tellurium in the 800 °C-treated samples that could be explained by the loss of a volatile species. Studies have described volatile tellurium species that are formed at elevated temperatures under oxidizing conditions [23–25].

##### *Spherical CPG*

Similar experiments were conducted for the spherical CPG material. These results are presented in Fig. 1b. The spherical CPG blank in this case showed an elevated zirconium concentration. The metal-loaded material contained about 1.5 times more metal than expected based on



**Fig. 1** ICP/OES analysis of solutions resulting from total dissolution of **a** irregular CPG, **b** spherical CPG, and **c** core-shell silica. Each plot shows results for a material blank, metal-loaded material that has not been heated, and metal-loaded material that has been heated at 600 or 800 °C for either 24 or 72 h. The concentrations shown are relative to the theoretical loading quantity that would be expected from filling the material pore volume with the metal-loading solution (see text for details)



filling of the spherical CPG pores alone (Table 1). A similar result was noted with irregular CPG and seems to indicate surface coating. Although the WDS studies indicated that the gold concentration was elevated, total dissolution showed the overall gold concentration was in line with the majority of other metals. This seems to indicate

that the gold was present in localized in spots on the surface, a result consistent with the secondary electron microscopic imaging. The high levels of zirconium in the spherical CPG blank explained the apparent elevation of this metal concentration in the metal-loaded CPGs. Again, as seen previously for the irregular CPG, the results

showed elevated niobium and lower rhenium concentrations. Selective loading of niobium could explain the elevated concentration of this metal. Rhenium was depleted in the metal-loaded materials that were subjected to heat, again suggesting loss of volatile rhenium species.

#### Core-shell silica

The core-shell silica also was dissolved and analyzed by ICP/OES. The results are presented in Fig. 1c. The core-shell blank was clean, showing that the material did not contain interfering metals. The loading for most low-boiling-point metals was approximately three times higher than what would be expected from filling the pores in the shell of the material (see Table 1). As with the other materials, this seems to be related to surface coating. The larger deviation from theoretical conditions than seen with the CPGs could reflect the higher exterior surface area per gram of the monodisperse small spherical particles (2.6  $\mu\text{m}$  diameter) compared to the surface areas of the CPGs. With the exception of tin, the metals have similar, fairly consistent concentrations. Selective loading could explain the high concentration for tin.

#### Selective loading of niobium and tin

To gain insight into the higher loading of niobium on the CPGs and tin on the core-shell silica, concentration measurements were performed on the load solutions, both before and after filling the material pores. Provided that filling of the pores is nondiscriminatory (i.e., does not discriminate either for or against the metals), the concentrations will be the same in the original load solution (before uptake) and the solution remaining after filling the material pores (after uptake). Figure 2 presents data for the analysis of a “before” and “after” load solution used to prepare irregular CPG material. The concentrations before and after pore filling were approximately equivalent for all

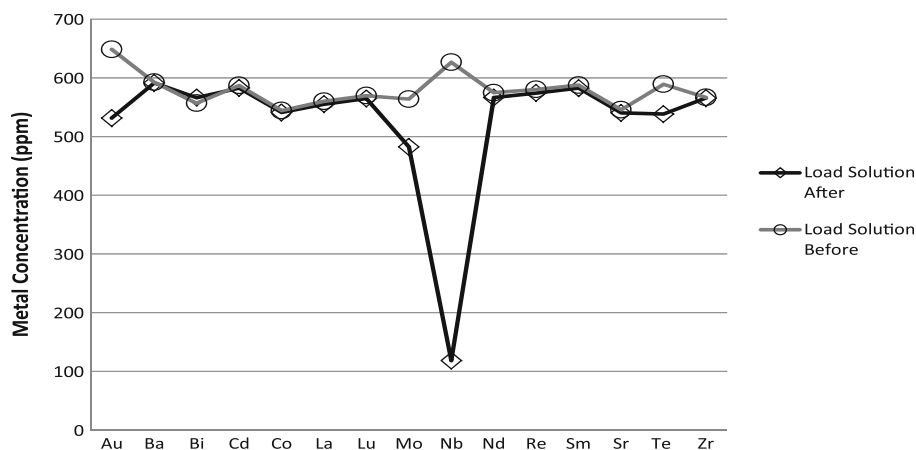
metals except niobium, as would be expected for passive loading (i.e., no discrimination). On the other hand, niobium was depleted in the “after” solution, indicating selective loading by the CPG materials. Calculations show that amount of niobium depletion accounted for slightly more (by about 40 %) than the enhanced levels observed for the total dissolution studies. However, these were independent trials and only represent a single data point. Evidence overall seems to indicate that selective loading of the niobium occurs on the CPG materials. The far smaller differences shown in the before and after solutions in Fig. 2 for gold, molybdenum, and tellurium also are suggestive of selective metal loading; however, these differences could not be verified by examination of the total dissolution data of the loaded material.

Similar experiments were conducted for the core-shell silica load solutions. These results indicated equivalent concentrations of the metals for the “before” and “after” load solutions with the exception of a diminished tin concentration that remained in the solution after filling the material pores. In this case, the quantity of tin that was depleted from the “after” load solution was in excellent agreement with the additional quantity of tin found on the loaded core-shell material, again suggesting that tin is selectively loaded on the core-shell silica.

#### Loading reproducibility

One critical requirement for producing synthetic nuclear explosion debris is the ability to reproducibly prepare the material. Likewise, it is important to know the homogeneity of the material within each batch. Both these parameters need to be characterized if the material is to be used to develop analytical methods. To assess the inter-batch reproducibility, the irregular CPG was prepared in three separate batches (0.50 g), and each batch was subjected to heat treatment at 800  $^{\circ}\text{C}$  for 72 h. The resulting material was then dissolved and analyzed using ICP/OES.

**Fig. 2** ICP/OES analysis of metal-loading solutions before and after exposure to irregular CPG. All metals except niobium have similar concentrations before and after exposure to the CPG, indicating loading was passive. On the other hand, niobium was depleted, indicating selective loading (see text for details)





Values for rhenium were excluded from reproducibility calculations because of its severe loss upon heat treatments. The RSD of each metal concentration was calculated and averaged for 15 metals. This study indicated an inter-batch RSD of 7.8 %, ranging from 10.4 % for gold, to 3.0 % for cadmium. This indicates that preparation of the material is highly reproducible.

Intra-batch reproducibility also was examined using the 72-h 800 °C-treated irregular CPG material by sub-sampling in triplicate one of the batches used for the inter-batch study described above. Samples were representatively taken using the draw-and-quarter approach, and then dissolved and analyzed. Results indicate the RSD of the three intra-batch analyses for 15 metals was 0.84 %, ranging from 2.4 % for gold to 0.4 % for zirconium. This study indicates that material sampled (20 mg) within a production batch (total of 0.5 g) was highly homogeneous. The quantities reported are important because heterogeneity may be observed for techniques requiring far smaller micro-quantities (e.g., single particle or a spot on a particle as exemplified by WDS analysis). The instrumental precision also was determined because this factor contributed to the RSDs reported above. This experiment analyzed one of the dissolved inter-batch samples in triplicate. An RSD of 0.69 % for the metals, ranging from 1.8 % for gold to 0.1 % for cadmium, was obtained.

#### Metal leach studies

Leach results for the 24 h period were particularly informative and were chosen for presentation here. For moderate leach conditions in general, we found that the 5 % nitric acid/5 % hydrochloric acid mixture was more effective at leaching metals than 5 % nitric acid alone. Therefore, to simplify the data presentation further, only the 5 % nitric acid/5 % hydrochloric acid leach is shown for the moderate leach conditions below.

#### *Irregular CPG*

The heat treatments were intended to facilitate transformation of metals to intractable species that would more closely emulate the speciation found in fallout particles. A number of factors could contribute to the inability to extract metals from metal-loaded CPG—strong adsorption, the formation of insoluble chemical species (e.g., oxides), physical sequestration resulting from pore collapse, or incorporation into the glass matrix [28].

Figure 3 shows the leach results for the irregular CPG. Figure 3a shows the quantities of metals leached into distilled water after 24 h of exposure. The quantity values are a ratio of the metal amount leached compared to the theoretical amount expected based on material pore volume

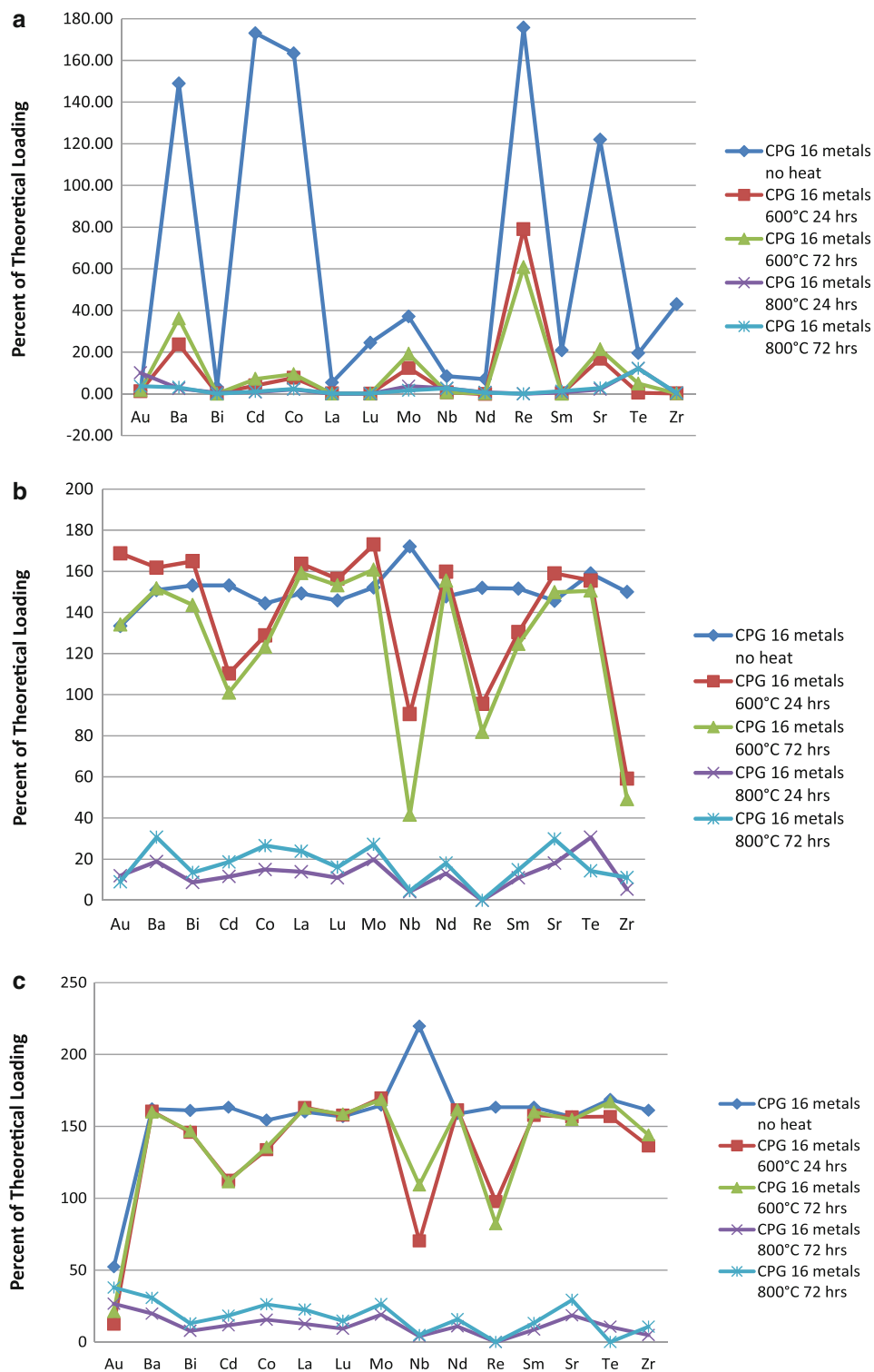
filling, and assuming complete leaching of the metals. These data are presented in this format to allow direct comparison to the total dissolution data shown in Fig. 1. Figure 3a shows there were only a few metals that were effectively leached from the non-heated material (i.e., barium, cadmium, cobalt, rhenium, and strontium) using the weakest leach treatment. The other metals were tightly bound to the silica matrix and were not effectively leached by water. Interestingly, after subjecting the loaded CPG to the mildest heat treatment (600 °C for 24 h), all metals with the exception of rhenium became intractable, and the presence and/or the extractability of rhenium was significantly reduced. These experiments clearly show the formation of recalcitrant forms upon exposure to heat.

Figure 3b shows the leach experiment performed using a moderately strong leach solution consisting of 5 % nitric acid/5 % hydrochloric acid. This experiment demonstrated the metals were efficiently extracted from the metal-loaded material that was not heated. Materials heated to 600 °C, however, showed significant reduction in the amounts of niobium, zirconium, and possibly cadmium that could be extracted. The lower quantities of extracted rhenium probably resulted from loss as a volatile product, as noted during the total dissolution studies. For metal-loaded CPG materials that were heated to 800 °C, there is a striking reduction in the extractability of all metals; this result clearly demonstrates the formation of recalcitrant forms. Figure 3c shows results of a strong leach using 50 % nitric acid. The lower amounts of gold compared to the moderate leach likely reflect the absence of chloride complexant provided by hydrochloric acid. Interestingly the strong leach was capable of releasing more niobium from the non-heated material compared to the moderate leach; we previously determined this element was elevated in concentration relative to the other elements during the total dissolution studies. In contrast to non-heated material, examination of the 600 °C-treated material again verifies that niobium is present in a form that is less effectively leached. Similar to results obtained with the moderate leach experiment, Fig. 3c shows that, even with the strong 50 % nitric acid leach, only very small amounts of metals were leached from materials heated to 800 °C, again emphasizing that the metals were extremely intractable. The strong leach solution was capable of efficiently leaching the zirconium from the samples treated at 600 °C, whereas the moderate leach solution could not.

#### *Spherical CPG*

Results similar to the irregular CPG were obtained for the spherical CPG leach experiments as shown in Fig. 4. Of the high-boiling-point metals loaded on the spherical material, water effectively leached only cobalt and rhenium from the

**Fig. 3** ICP/OES analysis of solutions resulting from 24 h leaches of irregular CPG (blank), metal-loaded irregular CPG that has not been heated, and metal-loaded irregular CPG that has been heated at 600 or 800 °C for either 24 or 72 h. Leach solutions are **a** distilled water, **b** 50 % nitric acid/50 % hydrochloric acid, and **c** 50 % nitric acid



non-heated material (Fig. 4a). Heating generally caused the formation of species that were not effectively extracted with water for most metals studied, although the quantity of water-extractable molybdenum appeared to increase in the 600 °C-treated samples compared to the non-heated control. As shown in Fig. 4b, moderate leach conditions

were far more effective at solubilizing metals from the samples treated at 600 °C, although niobium, and to a lesser degree zirconium, were not effectively leached presumably because of their strong association with the CPG material. Rhenium was leached from the non-heated material but not from the heated materials, an observation

that is consistent with loss of a volatile oxide upon heating. Consistent with results obtained with the irregular CPG (although the effect was not quite as pronounced) most metals showed a notable decrease in extractability on materials heated to 800 °C compared to those heated to 600 °C. The single exception to this was the molybdenum in a sample treated at 800 °C, which showed similar extractability as the material treated at 600 °C and the non-heated controls. The results for the strong nitric acid leach solution are very similar to those for the moderate leach conditions (Fig. 4c).

#### *Core-shell silica*

The core-shell material was subjected to the same leach conditions as described above. As shown in Fig. 5a, limited amounts of barium, cadmium, cobalt, and strontium (about one-third of the total present) were leached using water from the non-heated control material. Heated materials had higher quantities of water-soluble silver and lower quantities of barium, cadmium, cobalt, and strontium compared to the non-heated control. The other metals were not effectively leached from the material using water. Not surprisingly, moderate leach conditions (see Fig. 5b) were more effective at leaching the metals. The moderate leach conditions show that progressively more extreme heat treatments lead to larger proportions of intractable metal forms. Figure 5b differentiates between samples being exposed to the most severe heat condition (800 °C and 72 h) from the milder treatment (600 °C for 24 h). This difference is most pronounced for tin, an element that was determined previously to have an enhanced concentration relative to the other elements. For tin, clear differences are observed between the 600 and the 800 °C conditions, and further, the moderate leach conditions could differentiate between the 24 and 72 h exposures within the 800 °C-treatment. The strong 50 % nitric acid leach effectively extracted most of the metals studied as shown in Fig. 5c. A pronounced temperature effect that distinguishes between core-shell silica treated at 600 and 800 °C is again observed for tin. In the strong leach case, however, differences are observed between the 24 and 72 h treatment periods within the 600 °C-treatment group, rather than the 800 °C-treatment group.

#### Suitability as a nuclear explosion debris surrogate

The described methodology has several important advantages for producing surrogate nuclear explosion fallout particles. Foremost, the approach is straightforward, versatile, and easy to execute. Solution-based methods should be easier to implement for loading radioactive isotopes compared to gas-phase loading. In addition, quantitative loading is relatively easy to control in solution. Other

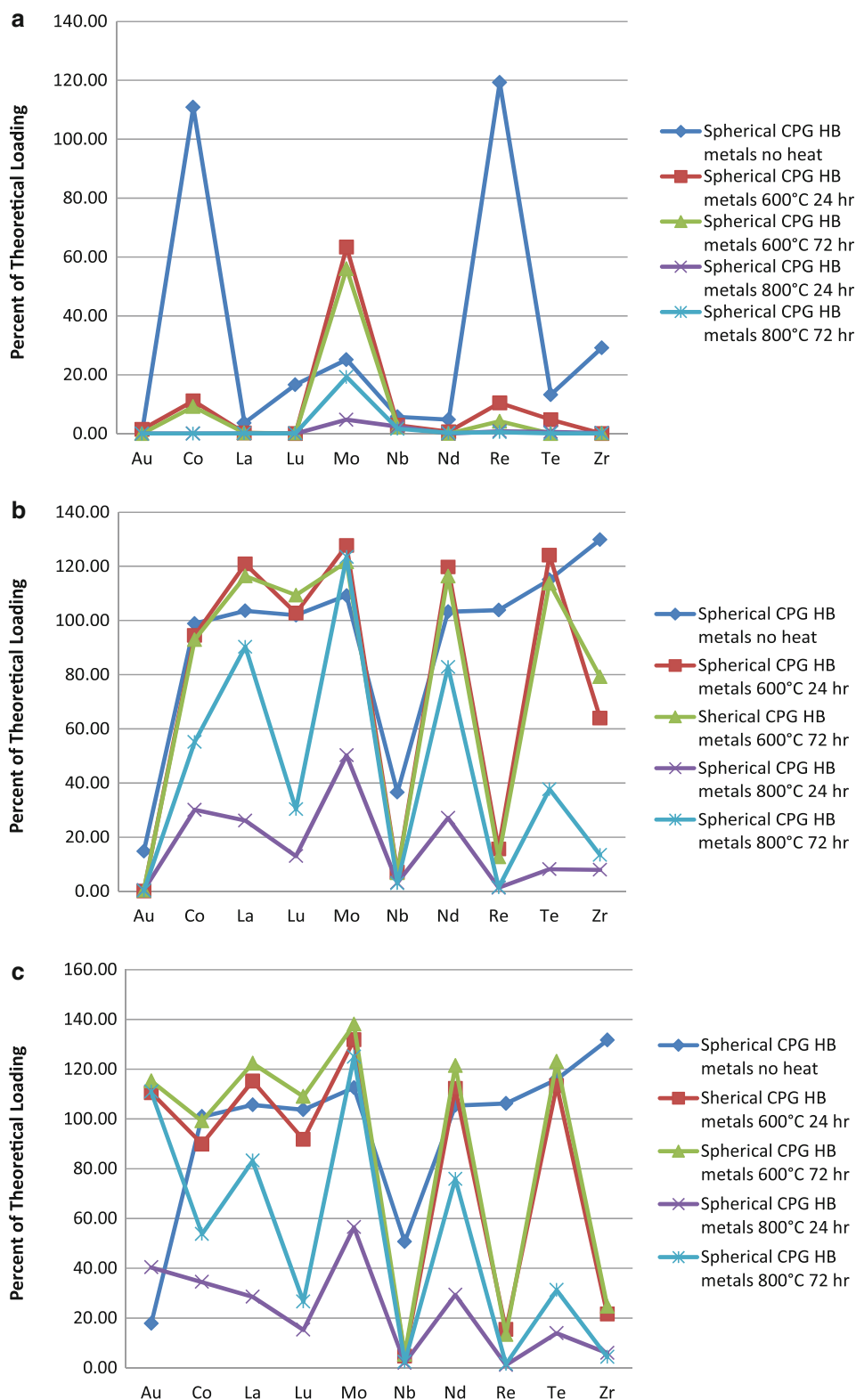
advantages are the preparation process, which is highly reproducible, and the homogeneity of the material, as judged by analysis of the metal-loaded irregular CPG. Heat treatment of the loaded materials shows that recalcitrant species are produced, as would be expected in the actual nuclear fallout. Sequestration and immobilization within the material described makes this a far more desirable surrogate for analytical methods development than surface-spiked materials because of the more accurate representation of the real material.

An additional attractive feature of the material is that silica-based surrogate debris particles represent fallout produced under a wide range of scenarios. Silica-based debris would be expected not only from surface bursts over desert sand, but also from construction materials found in an urban setting. An urban blast would be expected to form silica-based debris from numerous materials including glass, concrete, brick, sandstone, granite, slate, and the stone/sand/gravel aggregate contained in asphalt.

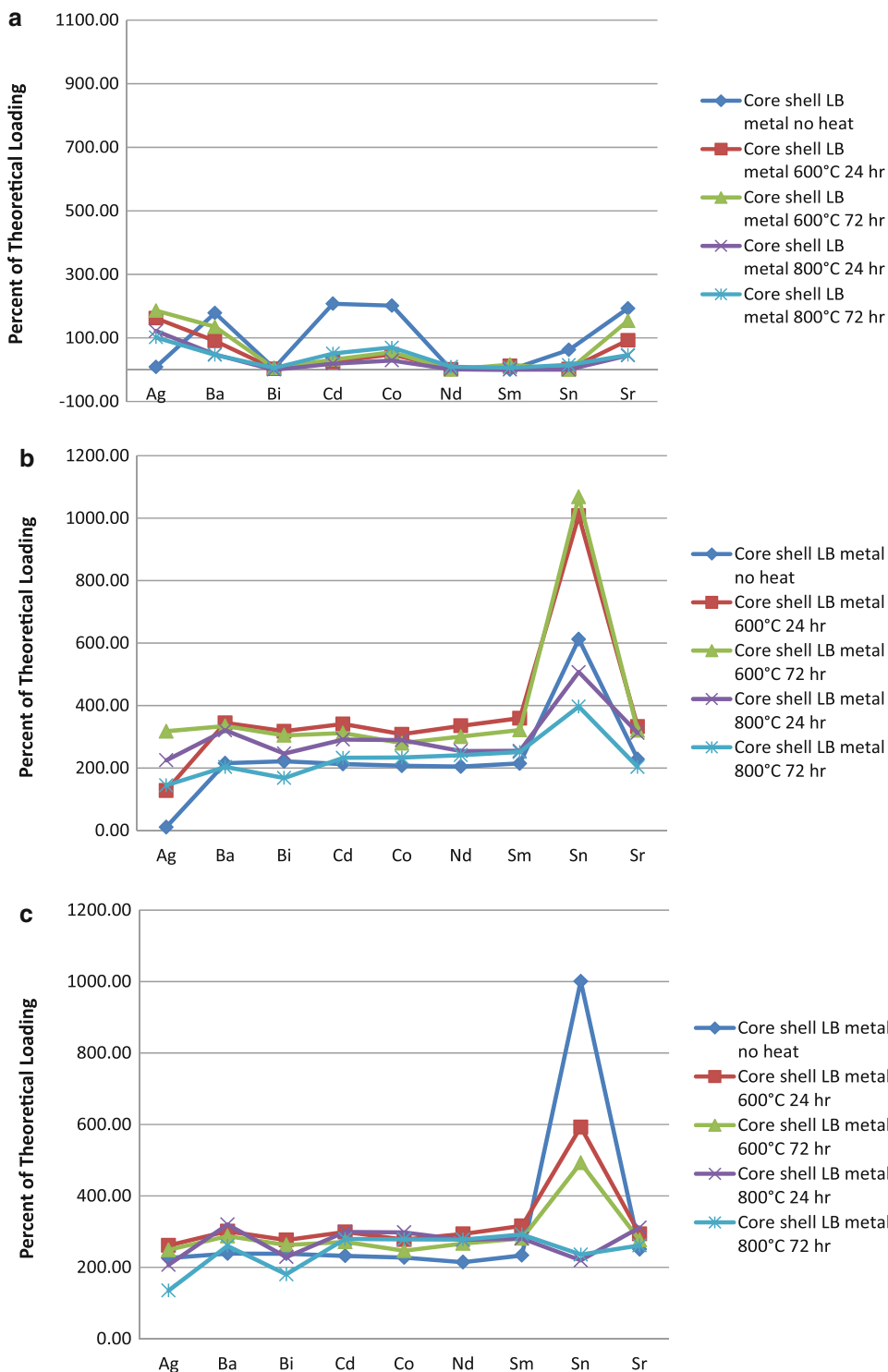
Although the materials described have many advantages, there are some potential limitations as well. Silica-based particles cannot completely represent debris with incorporated materials that would arise from nuclear detonations, especially for detonations in urban settings. Investigation of other porous chromatographic materials besides silica (e.g., alumina and possibly zirconia) might address some of this gap, but to fully address this issue, it may be necessary to focus on materials other than porous chromatographic materials. In addition, although the temperatures used were near the maximum the materials could withstand without fusing, these test conditions are mild compared to conditions that would be encountered in an actual event. Certain other high-energy production techniques may better emulate the extreme temperature and pressure conditions within a nuclear fireball. A final limitation is the limited availability of core-shell silica substrate. Although CPGs are available in a wide variety of sizes, the core-shell silica material is commercially available only in limited quantities and in a narrow range of low micron diameter sizes, and bulk production of the material currently would be cost prohibitive.

Although the scope of this study was limited to particle synthesis, many other forms of nuclear explosion debris exist. One such example is Trinitite, the heterogeneous glass left after the 1945 Trinity atomic bomb test [26, 27]. Producing surrogate composite material similar to Trinitite will involve combining methods described in this paper with additional methods for nuclear explosion debris synthesis (e.g., bulk glass formation methods). Versions of surrogate nuclear explosion fallout particles described here are anticipated to be used as a seed material to add relevant heterogeneity during glass production to produce more complex composites.

**Fig. 4** ICP/OES analysis of solutions resulting from 24 h leaches of spherical CPG (blank), metal-loaded spherical CPG that has not been heated, and metal-loaded spherical CPG that has been heated at 600 or 800 °C for either 24 or 72 h. Leach solutions are **a** distilled water, **b** 50 % nitric acid/50 % hydrochloric acid, and **c** 50 % nitric acid



**Fig. 5** ICP/OES analysis of solutions resulting from 24 h leaches of core–shell silica (blank), metal-loaded core–shell silica that has not been heated, and metal-loaded core–shell silica that has been heated at 600 or 800 °C for either 24 or 72 h. Leach solutions are **a** distilled water, **b** 50 % nitric acid/50 % hydrochloric acid, and **c** 50 % nitric acid



**Conclusions**

This study describes preliminary loading and characterization studies associated with synthesis of surrogate nuclear explosion debris particles using porous chromatographic substrate materials. A variety of particles that included both

irregular and spherical morphologies were prepared. Materials were easily prepared by filling pores with an aqueous load solution that contains metals, removing the water with gentle heat, and then forming intractable forms of the loaded metals by heating (600 or 800 °C) in air for periods up to 72 h. Metals of interest were loaded on CPG

materials in mixtures that either contained a broad range of metals (irregular CPG), or as mostly high-boiling-point metals (spherical CPG). The materials resulting after temperature treatments should have homogeneous metal distributions characteristic of particles formed early in the fallout genesis process. In addition, core–shell silica was investigated as a substrate for preparing particles that contained a surface coating of low-boiling metals to emulate debris particles formed later in the process.

Studies demonstrated that metal loading was not restricted to the material pores, but significant surface coating also occurred. Most metals were passively loaded; however, pronounced elevation in the concentrations of niobium and tin were observed on the silica-based materials. Metal-loading experiments verified that these metals were selectively removed from the load solution. Leach experiments verified that the temperature treatments formed recalcitrant species for many metals, and also highlighted the incremental formation of recalcitrant species resulting from exposure of the materials to higher temperatures or, in some cases, to increased exposure time to elevated temperatures. Batch-to-batch reproducibility was high (the RSD was 7.8 %), as was the intra-batch homogeneity (the RSD was 0.84 %), making these materials viable candidates for analytical methods development. We anticipate future materials that contain appropriate radioisotopes will find use as stand-alone materials to emulate nuclear debris fallout or for production of additional materials. For example, these materials could be used as starting substrates for high-energy production approaches or as a seed material for making more complex nuclear explosion debris forms.

This study describes the use of porous chromatographic materials for producing nuclear debris fallout particles. This is an entirely novel use of porous silica-based chromatographic materials that are commonly used in the chromatographic community. In addition to providing a critically important material for use in developing analytical methods in the nuclear forensics field, this study also serves to further expand the use chromatographic materials into novel application areas.

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